

TWO-STAGE LIQUEFACTION OF WYOMING SUB-BITUMINOUS COAL - EFFECT OF SYNGAS AS REDUCING GAS

L.K. Lee, V. Pradhan, R.H. Stalzer and A.G. Comolli
Hydrocarbon Research, Inc.
100 Overlook Center, Suite 400
Princeton, New Jersey 08512

Keywords: Liquefaction, Sub-bituminous coal, Water-gas Shift Reaction

INTRODUCTION

The production of hydrogen constitutes one of the major operating cost components of a coal liquefaction process. Alternative sources of hydrogen such as synthesis gas, a mixture of CO/H_2 coming directly from a gasifier or steam reformer with minimum processing, can potentially improve the economic of a liquefaction plant. Also, it is known that in the presence of an alkali salt, $\text{CO}/\text{H}_2\text{O}$ is very effective in solubilizing high oxygen containing low rank coals at relatively mild severity conditions^{1,2}.

Non-alkali promoters, like iron⁴, cobalt/molybdate⁴⁻⁶ salts, were found to be active in enhancing the production of hydrogen through the water-gas shift (WGS) reaction. With the addition of H_2S , the presence of promoters had only a minor effect on coal conversion.⁵ In a two-stage direct coupled operations, in which activity of the second stage hydroprocessing catalyst can be severely reduced by alkali salts, it is necessary to explore non-alkali promoters for the WGS reaction. This paper discusses the work using a dispersed and a supported non-alkali promoter to catalyze the coal solubilizing step using a mixture of syngas and water.

PROCESS AND BENCH UNIT DESCRIPTIONS

Two-stage liquefaction tests were carried out in a bench scale continuous flow unit of nominal capacity of 1 Kg/h of coal feed. This unit was configured with two equal volume, fully backmixed reactors. Depending on the form of catalyst used, dispersed or supported, the first stage was operated either as a slurry reactor or an ebullated bed reactor. On the other hands, the second stage was utilized as an ebullated bed reactor. A simplified process flow diagram is shown in Figure 1. Coal dissolution occurred in the first stage in the presence of H_2 or CO/H_2 , while the primary liquids were further upgraded in the second catalytic stage under typical hydroprocessing conditions.

An interstage separator was used to remove excess syngas/water, light distillates and gaseous products generated from the coal solubilizing stage. Products from the second stage reactor were recovered as Separator and Atmospheric Still Overheads. Bottom materials from the Atmospheric Still, consisting of heavy distillates, unconverted coal and ash, was subjected to pressure filtration. The pressure liquid was recycled for slurring the coal feed. Sulfur additives can be injected to both stages.

CATALYST SCREENING

Several WGS promoters (sodium carbonate, sodium aluminate, iron oxides/DMDS, ammonium heptamolybdate(AHM)/DMDS, Amocat 1A/DMDS, Shell 317/DMDS) were evaluated using a 20 c.c. microautoclave at 399°C and 5.5 MPa cold CO pressure with and without solvent. CO and H_2O was charged at a molar ratio of 1/1. These catalysts were ranked according to the degree of the CO conversion. The relative activity ranking is:

Amocat 1A, Shell 317 > AHM > K_2CO_3 , $\text{NaAlO}_2 \gg \text{Fe}_2\text{O}_3$

with or without solvent, as illustrated in Figure 2. Higher conversions were observed for tests with no solvent, it was probably due to better interaction between the reactants and the catalyst.

BENCH SCALE TESTS

Two bench runs were conducted to compare the activity of AHM and Shell 317 N/Mo extrudate catalyst as promoter for the coal solubilizing stage. In CMSL-03, AHM was premixed in the feed slurry at a concentration equivalent to 1500 wppm of Mo on a dry coal basis, while Shell 317 was loaded into the first reactor in CMSL-04. Due to the presence of the supported catalyst, the fluid volume in the first stage was 25% smaller in CMSL-04. Therefore, for the same feed rate a higher space velocity through the first reactor was anticipated in CMSL-04. The run conditions and performance of these two runs are compared in Table 1.

In the case of AHM, replacing H_2 with $CO/H_2/H_2O$ as reducing gas resulted in 2.5-3.0 W% higher coal conversion and a similar increase in distillate yield. Under similar operating conditions, in the presence of Shell 317, the improvement in performance by using syngas was less significant, less than 1.0 W%.

In comparing the performance of the first stage catalyst, AHM vs Shell 317, it is necessary to consider the different in fluid volume associated with each catalyst. The effective fluid volume was 25% lower in the case of the supported catalyst. As a result, at the same feed rate, both the coal conversion and distillate yield were lower when Shell 317 was used. Coal conversion reduced from 92.0 W% in CMSL-03 to 87.6 W% in CMSL-04, while the distillate yield declined from 64.6 to 58.5 W% under similar process conditions. However, as anticipated, Shell 317 was more effective in removing heteroatoms. Nitrogen removal was 10 W% more effective with Shell 317 than when AHM was used.

FIRST STAGE PRODUCTS

The first stage reactor samples exhibited a similar trend as the two stage products in term of conversion and product qualities, as shown in Table 2. The first stage coal conversion was higher in CMSL-03 than that of CMSL-04. Due to the hydrogenation function of the supported catalyst, both the solid and liquid products were richer in hydrogen and lower in heteroatoms.

Approximately, half of the distillates were generated from the first stage. The first stage distillates were heavier and contained higher boiling materials when syngas/water was used, as shown in Table 3. In CMSL-03 the H/C ratio declined from 1.65 and 1.59 when H_2 was replaced by CO/H_2 . It seems that the removal of nitrogen was more effective with CO/H_2 -AHM combination. The nitrogen content of the first stage distillate, 0.057 W%, was 3.8 times lower than when H_2 was used. However, such improved performance with CO/H_2 was not observed when supported catalyst was used as promoter.

ACKNOWLEDGEMENT

HRI wishes to acknowledge the financial support of the U.S. Department of Energy under the Contract No. DE-AC22-93PC92147. Ms. Sally Kornfeld and Dr. Edward Klunder provided helpful comments.

REFERENCES

1. Cassidy, P.J., Jackson, W.R., Larkins, F.P., Louey, M.B. and Sakurovs, R.J., Fuel Processing Tech. 1986, 14, 231-246.
2. Porter, C.R., Knudson, C.L. and Rindt, J.R., ACS Div. Fuel Chem. Preprint, 1986 31 (4), 70-76.
3. Lim, S.C., Rathbone, R.F., Givens E.N. and Derbyshire, F.J., ACS Div. Fuel Chem. Preprint, 1993, 38 (2), 618-625.
4. Ng, F.T.T. and Tsakiri, S.K., Fuel 1993, 72, 211-215.
5. Amestica, L.A. and Wolf, E.E., Fuel 1986, 65, 1226-1232.
6. Nowok, J. and Stenberg, V.I., ACS 1987, 32 (1), 628-636.

Table 1 Performance on the Bench Tests

<u>Process Conditions</u>	CMSL-03 1	CMSL-03 2	CMSL-04 1	CMSL-04 2
1st Stage:				
CO/H ₂	0/100	75/25	0/100	0/100
Temperature, °C	388	388	388	427
Catalyst	AHM	AHM	Shell 317	Shell 317
2nd Stage:				
CO/H ₂	0/100	0/100	0/100	0/100
Temperature, °C	427	427	427	427
Catalyst	Shell 317	Shell 317	Shell 317	Shell 317
<u>Process Performance, W% maf coal</u>				
Coal Conversion	89.5	92.0	86.8	87.6
514°C Conversion	87.2	89.9	84.6	84.5
C1-C3	6.50	6.56	6.30	7.65
C4-524°C	61.6	84.6	57.6	58.5
H ₂ Used	7.82	7.73	8.10	9.61
HDN	75.9	84.8	96.9	95.1

Table 2 Analysis of First Stage Reactor Samples

<u>Process Conditions</u>	CMSL-03 1	CMSL-03 2	CMSL-04 1	CMSL-04 2
Coal Conversion, W%	90.3	84.1	79.5	77.5
H/C Ratio				
Filter Liquid	1.23	1.22	1.36	1.25
Filter Solid	0.57	0.65	0.94	0.89
N in Filter Liquid	0.57	0.50	0.22	0.35

Table 3 Analysis of First Stage Separator Overheads

<u>Process Conditions</u>	CMSL-03 1	CMSL-03 2	CMSL-04 1	CMSL-04 2
API Gravity	26.9	22.9	31.3	25.2
IBP, °C	85.0	83.3	88.3	95.0
FBP, °C	414	422	427	431
ASTM D-86 Distillation, W%				
IBP-177°C	14.1	12.4	35.22	23.7
177-260°C	10.3	10.5	9.43	10.5
260-343°C	51.6	45.6	26.7	27.5
343°C				
Elemental Analysis, W%				
Carbon	85.56	86.00	86.62	86.84
Hydrogen	11.74	11.37	12.67	11.67
Sulfur	0.079	0.086	0.015	0.043
Nitrogen	0.22	0.057	0.075	0.196
H/C Ratio	1.65	1.59	1.76	1.61

[illegible]

Polymer	No Solvent (%)	With Solvent (%)
None	12.5	8.5
PzCO ₃	5.5	3.5
Na ₂ CO ₃	14.5	14.0
NaAlO ₂	17.0	11.0
A-9M	28.0	17.0
NIMA	35.0	19.0
C ₆ M ₆	29.5	30.5
C ₆ M ₆	34.5	15.5